Cork as a sustainable carbon source for nature-based solutions treating hydroponic wastewaters – Preliminary batch studies

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HIGHLIGHTS

- The reuse of local by-products like cork allows preservation of natural capital.
- Cork has the potential to enhance denitrification in nature-based solutions.
- As particle size increases, the release of carbon becomes slower along time.
- Estimations showed that 1.8 m³–3.9 m³ of hydroponic wastewater could be treated.
- Cork particle size is a key parameter to design natural denitrification solutions.

GRAPHICAL ABSTRACT
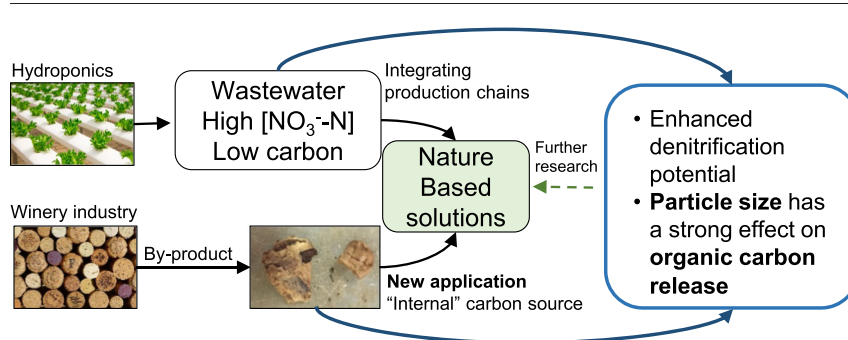
ABSTRACT

Reusing by-products is an important strategy to ensure the preservation of natural capital and climate change mitigation. This study aimed at evaluating the potential of cork granulates, a by-product of winery industry, as an organic carbon (OC) source for the treatment of hydroponic wastewaters. First, chemical characterization was performed and discussed. Secondly, batch studies were performed using synthetic hydroponic wastewater to understand the role of particle size (PS), pH and contact time (CT) on the release of OC. The suberin is the major compound, representing >50%. It was noticed that a variance on the content of suberin across species, within the same species and depending on the extraction part (belly, cork and back) could be expected. >60% of the sample is composed by carbon while <1% was nitrogen (high C:N ratio), indicating a low risk of releasing organic nitrogen. The statistical results suggested that the main effect of PS on the release of OC is greater than both, CT and pH. The chemical release of OC gets slower with time, being this effect greater as the PS increase. Moreover, estimations showed that using the 4 mm PS, the amount of water treated would be twice the amount if the 8 mm PS had been used. The PS seems to play an important role at design nature-based solutions (NBS) focused on denitrification. The surface response methodology indicates a significant negative interaction between CT and PS suggesting that the mathematical model could be used for further optimization studies. The reuse of organic by-products as filter media seems to be an economic and environmentally friendly alternative to enhance

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denitrification in NBS, while preserving natural capital. However, further real scale and long-term experiments are needed to validate cork's potential as an "internal" OC source for NBS.

1. Introduction

In the past years, the use of urban and soilless agriculture is becoming more common to supply the ever-increasing food demand and to deal with water and land scarcity, increasing the risk of water pollution. Wastewater from soilless agriculture, besides having high concentration of nitrates and phosphates is usually drained and discharged to the environment without proper treatment (Prystay and Lo, 2001). The leaching of N and P causes several environmental impacts such as, groundwater pollution, eutrophication of surface waters and ecosystem biodiversity losses. Therefore, the treatment of wastewaters generated by soilless agriculture is a must as it may play an important future role, with regards of ensuring food security, sustainable management of water resources and environmental protection, once this type of agriculture is implemented, both in urban and rural environments.

Conventional treatments such as reverse osmosis and ion exchange membranes were highly efficient, although have high maintenance and operation costs (Koide and Satta, 2004; Gagnon et al., 2010; Park et al., 2015). Therefore, NBS, namely, constructed wetlands (CWs) and biofilters, may represent a sustainable and low-cost alternative for the removal of nitrogen from hydroponic wastewaters before discharge (Park et al., 2008; Gagnon et al., 2010; Abbassi et al., 2011; Park et al., 2015).

However, nitrogen removal from hydroponic wastewaters by NBS can be a challenge, since this water is known to have high concentration of nitrates and, at the same time, low carbon content (Prystay and Lo, 2001). The availability of carbon is one of the main limiting factors regarding the efficiency of biological denitrification (Vymazal, 2007; Mutsvangwa and Matope, 2017). According to Mutsvangwa and Matope (2017) wastewaters with low carbon to nitrogen ratio, usually require an external carbon source to achieve denitrification. However, the use of external carbon sources such as, methanol, ethanol, acetic acid and fructose besides increasing operational costs can cause negative environmental impacts (Park et al., 2008).

Therefore, alternative organic materials such as, plant biomass (Wen et al., 2010; Zhang et al., 2014), flower straws (Chang et al., 2016) and plant pruning (Park et al., 2008) have been proposed as external carbon sources to enhance denitrification in NBS, mainly because of their low cost, availability and renewable biomass. In addition, in the past 5 years, authors have shown the potential of roots exudates as a carbon source for denitrification in CWs (Zhai et al., 2013; Chen et al., 2016; Wu et al., 2017).

Moreover, some authors have suggested the use of organic filter media to enhance denitrification, such as, woodchip bioreactors (Nordström and Herbert, 2017), green walls built with coconut fibber and light expanded clay (Masi et al., 2016) and green walls with Coco coir (Prodanovic et al., 2017). Results of Prodanovic et al. (2017) indicated that biological processes are enhanced by the addition of organic filter media. The use of coco coir increased the retention time and the availability of OC, enhancing the microbiological removal process. On the other hand, the use of organic substrates can lead to an accumulation of total nitrogen in the effluent. The study of Masi et al. (2016) showed an increment of total Kjeldahl nitrogen when using coconut fibber and light expanded clay mixed, possibly due to the increment of retention time, which favours the release of organic compounds, such as organic nitrogen.

Nevertheless, reusing organic by-products, as filter media transforms, what was once an external source, into an integrated part of the system, reducing operational costs while preserving natural capital. In this regard, cork granulated seems to have potential to be used as a sustainable "internal" organic source for the treatment of hydroponic wastewaters.

Cork granulates by-product is generated from several operations of wine industry and is considered as a natural, renewable and biodegradable raw material (Olivella et al., 2011a; Sierra-Pérez et al., 2016). The cork oak trees are planted, the bark is stripped for the first time when tree is 20 to 25 years old. The next stripping is carried out every 9 to 12 years, with an expected productive life from 100 to 300 years depending on the tree's health (Jové et al., 2011; Olivella et al., 2013a). >80% of the world's cork is produced in Europe, being the annual production about 340.000 ton (Olivella et al., 2011a). However, the cork waste generated is around 50.000 ton (Olivella et al., 2011a), which represents approximately 15% of waste in relation to the total cork extracted.

Moreover, several researchers have shown the potential of cork to remove emergent pollutants such as, polycyclic aromatic hydrocarbons (Olivella et al., 2011a, 2011b, 2013a), phenanthrene (Olivella et al., 2013b), methyl orange (Krika and Benlahbib, 2015), ofloxacin (Crespo-Alonso et al., 2013), Biphentrin (Domingues et al., 2005) ibuprofen, carbamazepine and clofibric acid (Dordio et al., 2011) or heavy metals (Pintor et al., 2012). On the other hand, not much is known about the behaviour of cork regarding the release of OC and its potential to enhance denitrification in NBS.

The main goal of this paper was to investigate the potential of granulated cork as an OC source. The chemical release of OC can play an important role regarding the establishment of biofilm in natural wastewater treatments. Moreover, the chemical OC released by the substrate can enhance denitrification process while reducing the use of external carbon sources and thus, ensuring a long-term performance on pollutant removal, reducing operation costs and environmental hazard. The granulated cork was characterized (PZC, FTIR, chemical and elemental constitution) and batch studies were performed using synthetic hydroponic wastewater in order to understand the role of PS, pH and CT on the release of OC.

2. Materials and methods

2.1. Synthetic hydroponic wastewater

The composition of hydroponic wastewaters varies depending on the crops, type of fertilizers used for the nutritive solution, frequency of application, time of the year and type of system (closed or open). A literature research was made to establish a reliable range of contaminants to guide the preparation of synthetic hydroponic water (Table 1). The compounds used to prepare the solution were potassium Nitrate (KNO_3), calcium chloride dihydrate ($CaCl_2 * 2H_2O$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), sodium hydroxide (NaOH), magnesium sulphate heptahydrate ($MgSO_4 * 7H2O$) and zinc sulphate heptahydrate ($ZnSO_4 * 7H2O$). The hygroscopic compounds were dried at 105 °C for 4 h and all compounds were mixed with tap water. When it was necessary, the water was stored in a freezer at 10 °C in order to avoid losses of N-ammoniacal by volatilization. However, the water was not stored for >3 days. The wastewater was prepared five times during the experiment to provide the same initial concentrations of contaminants for all the treatments. All data and the standard deviation can be seen in Table 1.

Table 1
Composition of hydroponic synthetic wastewater (Adapted from Prystay and Lo, 2001; Koide and Satta, 2004; Huett et al., 2005; Taylor et al., 2006; Park et al., 2009; Gagnon et al., 2010; Gruyer et al., 2013; Dunets et al., 2015; Park et al., 2015).

Compounds	Unit	Synthetic hydroponic wastewater		Literature RANGE	
		Average ([a]SD$\pm$)		Min	Max
N total	mg/L	70.89 $\pm$ 1.1		2.8	122.0
NO_3^--N	mg/L	66.28 $\pm$ 1.0		10.0	414.0
NH_4^+-N	mg/L	4.61 $\pm$ 1.4		0.8	36.7
PO_4^{-3}-P	mg/L	11.01 $\pm$ 3.3		0.7	99.3
[b]K^+	mg/L	189.18		13.0	459.0
[b]Na^+	mg/L	83.00		83.0	108.0
[b]Ca^{2+}	mg/L	123.52		21.0	295.0
[b]Mg^{2+}	mg/L	90.00		10.0	105.0
[b]Cl^-	mg/L	41.00		3.9	80.0
[b]Zn^{2+}	mg/L	0.50		0.03	1.4
pH		9.6 $\pm$ 0.08		5.5	7.3
[c]EC	dS m^{-1}	2.2 $\pm$ 0.05		1.3	2.3
[d]SAR	meq L^{-1}	1.96		1.8	2.0

[a] Statistical deviation (SD) was performed using IBM SPSS.
[b] Concentration calculated by the amount of compound used (same for all water prepared).
[c] Electrical conductivity.
[d] SAR: the Sodium Adsorption Rate was calculated based on (Pescod, 1992). To determine the literature range, the SAR was calculated considering the values of Na^+, Ca^{2+} and Mg^{2+} found in the following papers: Koide and Satta, 2004; Park et al., 2009.

2.2. Cork preparation

For the present study, the "cork-wood" granulates extracted from the cork oak trees (*Q. suber*) were used. "Cork-wood" is a raw material with high density, which is not appropriate for the production of wine stoppers. This material does not go through any disinfection method (boiling process) and normally is reused raw as organic fertilizer. "Cork-wood" is a mixture of the denser part of the cork, which has part of the back of the cork bark (woody part), part of the belly (innermost part) and the one that is understood by cork. The cork used for this study was provided by the Catalan Cork Institute (ICSURO). The cork was washed 3 times with demineralized water, dried for 48 h at 105 °C and sieved to obtain PS of 4 mm and 8 mm.

2.3. Cork characterization

A Fourier Transform Infrared Spectroscopy (FTIR) test was performed using Cary 630 FTIR according to the internal protocol PNTM 7.5-54 by triplicates (Ortega-Fernández et al., 2006; Prades et al., 2010; Miranda et al., 2013). Chemical constitution analysis methods have previously been described by Jové et al. (2011). The elemental analysis of C, H, N and O were performed with 4 samples (replicates), using elemental analyser EuroVector EuroEA3000 equipped for analysis of CHNS.

The determination of PZC for each PS of cork (4 mm and 8 mm) was based on the immersion technique (adapted from Fiol and Villaescusa, 2009; Hafshejani et al., 2016). The pH value at the PZC was determined by adding 250 mL 0.1 M NaCl solution into a series of 500 mL plastic flaks. The initial pH of the aqueous solutions was adjusted in the range of 1–10 by the addition of HCl (0,5-1M) or NaOH (0,5-1M). After the pH adjustment, 15 g of cork were added to each flask and the suspension was shaken for 24 h, at 40 rpm and 22 $\pm$ 1 °C. The solution was finally filtered on 0.45 mm cellulose acetate membrane filter and the final pH was measured using digital pH meter (Metrhom) standardized by NBS buffers. The experiment was performed in triplicates. The variation of pH (ΔpH = initial pH – final pH) was plotted versus initial pH.

2.4. Batch studies

The batch studies were carried out at the Department of Bioscience - Aarhus University (Denmark). To evaluate the effect of PS and pH on the release of OC, the following experimental design was performed: Factor PS (levels 4 mm and 8 mm) and Factor pH (levels 3, 5, 7 and 9). The Kinetics experimental design considered PS as factors (levels 4 mm and 8 mm) and CT (levels 0.5, 1, 3, 12 and 24 h). All the experiments were performed in triplicates. Blank samples, without cork, were used as control.

The initial composition of the synthetic hydroponic wastewater was constant during the entire experiment (Table 1). Plastic flasks (250 mL) were used to mix the synthetic water and the cork granulate (PS 4 mm and 8 mm). Each flask was filled with five grams of cork and 50 mL of synthetic hydroponic wastewater, resulting in an adsorbent dosage of 100 g of cork per L^{-1}. The temperature during the batch essays was constant, approximately 20 °C ($\pm$1 °C).

2.4.1. Effect of PS and pH on the release of OC

The initial pH of synthetic hydroponic wastewater (SHW) was adjusted to different pH values (3, 5, 7 and 9) either with HCl (0,5-1 M) or NaOH (0,5-1 M) and the SHW was characterized in order to know if initial concentrations were in accordance with the expected range (Table 1). Initial values of OC were considered to be zero. The adsorbent dosage of 100 g L^{-1} was achieved adding the desired amount of adsorbent and aqueous solution into plastic flasks (250 mL). The suspensions were shaken at 40 rpm at 20 $\pm$ 1 °C during 24 h. The solutions were filtered and the final pH of filtered samples was measured using a HACH digital probe and the non-purgeable organic carbon (NPOC) was measured.

A factorial ANOVA (4×2) was performed in order to analyse main effects and interaction for significance of 4 mm and 8 mm PS and pH 3, 5, 7 and 9 on the release of OC. Post Hoc test (Tukey HSD 5%) were carried out just for the pH independent variable (>2 levels) in order to determine the significance of the differences between the means across the levels.

2.4.2. Kinetics

Kinetic experiments were conducted under pH 7, normally based in hydroponic wastewaters (Table 1), by varying the CT: 0.5, 1, 3, 12, 24 h following the methods previously described. After the pre-established CT, the samples were filtered using a cellulose membrane filter, and non-purgeable organic carbon (NPOC) analysis were performed.

A factorial ANOVA (5×2) was performed to analyse the effect of PS (4 mm and 8 mm) and CT (0.5, 1, 3, 12 and 24 h) on the release of OC. Post Hoc test (multiple comparisons – Tukey HSD 5%) were carried out just for the CT (>2 levels) to determine the significance of the differences between the means across the levels. In order to determine the specific relationships between both independent variables (PS and CT) across levels, an analysis of simple effects was conducted, using general linear model.

2.4.3. OC indicators

In order to analyse the data from the batch studies, 3 indicators are proposed. The description of the indicators can be seen below.

$$OC_I = NPOC_f * V$$

OC_I (mg) = mass balance or the mass of OC released. Where, $NPOC_f$ is the final concentration of non-purgeable organic carbon (mg L^{-1}) and V is aqueous volume of the sample (L).

$$OC_{II} = {OC_I}/{M}$$

OC_{II} (mg of OC/g of cork) = The amount of OC released per gram of cork. Where M is the mass of cork in the samples (g) (adapted from Crespo-Alonso et al., 2013; Hafshejani et al., 2016)

$$OC_{III} = {OC_I * 100}/{MC_i}$$

OC_{III} (%) = % of OC released related to total OC in the sample. Where MC_i is the initial mass of OC in the sample (mg). For MC_i calculation the initial mass of cork (mg) and the elemental analysis of carbon (%) were considered. The elemental analysis performed showed that 66% of the cork mass of samples was composed by carbon, regardless the PS (following the methodology described in Section 2.2 – cork characterization).

2.4.4. Statistics

As mentioned before, for both experimental stages an ANOVA factorial analysis was carried out using the software IBM SPSS Statistics (version 23), in order to understand the main effects of PS, CT and pH on the chemical release of OC. Only the indicator OC_I was used for statistical analysis.

Moreover, the effects on each factor have been individually analysed by a "trial and error" approach. Therefore, for the kinetic studies, the design of the needed experiments was carried out using Design Expert® (Design-Experts Software Version 7.0). The DoE technique allows verifying whether or not there is a synergistic effect between the variables on the final response (Montgomery, 2012; Formosa et al., 2012), and which parameters can influence the release of OC to a greater extent. The objective was to quantify the results according to the PS and CT, which are related to the kinetics. On this manner, a desirable OC_I can be obtained by varying the parameters under study (i.e.: PS and/or CT). The statistic approach was a response surface methodology (RSM), specifically a historical data to further perform an optimization process by using the results previously obtained. The analysis of DoE results is based on the analysis of variance (ANOVA) (Montgomery, 2012).

3. Results and discussion

3.1. Characterization of cork

In the following subsections the results from the analysis performed to characterize the cork samples will be presented and discussed.

3.1.1. FTIR

Cork is mainly composed by suberin and lignin (Miranda et al., 2013). Based on the FTIR spectra (Fig. 1), most characteristic absorption bands were between 2800 and 3000 cm^{-1}, corresponding to the link C—H of suberin (Cordeiro et al., 1998), similar to other previous results (Miranda et al., 2013).

The analysed samples showed other bands at 1738, 1630 and 1605 cm^{-1} corresponding respectively to the C=O bond of suberin and aliphatic acids, C=C bonds of suberin and lignin. Bands from 1600 to 1125 and 1087 to 1035 cm-1 were related, respectively, to different bonds of lignin and C—O bonds of polysaccharides (cellulose + hemicellulose) (Marques et al., 1994). As can be seen in Fig. 1, both PS (4 mm and 8 mm) showed similar behaviour regarding their bands and peaks. The heterogeneity of the samples can be explained by some differences between replicates.

3.1.2. Chemical constitution

The suberin was the major chemical compound, representing 51.3% of the total composition (Table 2). Together, suberin and lignin represented 65.4% of the total chemical composition of cork (Q. suber) analysed in this present study. Other authors showed similar results, where the suberin plus lignin of Q. suber ranged from 69.8% to 70.1% (Table 2). The lignin contents in Q. suber presented by Olivella et al. (2011a, 2011b) were, respectively, 2.2 and 1.8 times higher than the lignin content of Q. suber on our present study. The Q. suber content of suberin showed by Olivella et al. (2011a, 2011b) and by the present study, were respectively, 1.35, 1.54 and 1.8 times higher than Q. cerris (Olivella et al., 2011b). Those results suggest that might be a variance in the chemical constitution of cork within species and between species.

The variations within the same species might be related with the extraction part (belly, back and cork). As can be seen in Table 2, the content of suberin tends to be higher in the belly and cork than in the back part, fact that is in accordance with Jové et al. (2011). The samples of the present study are a mixture of back layer (woody part), belly (innermost part) and the one that is understood by cork, while the samples of Olivella et al. (2011a, 2011b) were just composed by the belly layer. Therefore, the higher content of suberin in our study in comparison with other works could be explained by the heterogeneity of our cork sources.
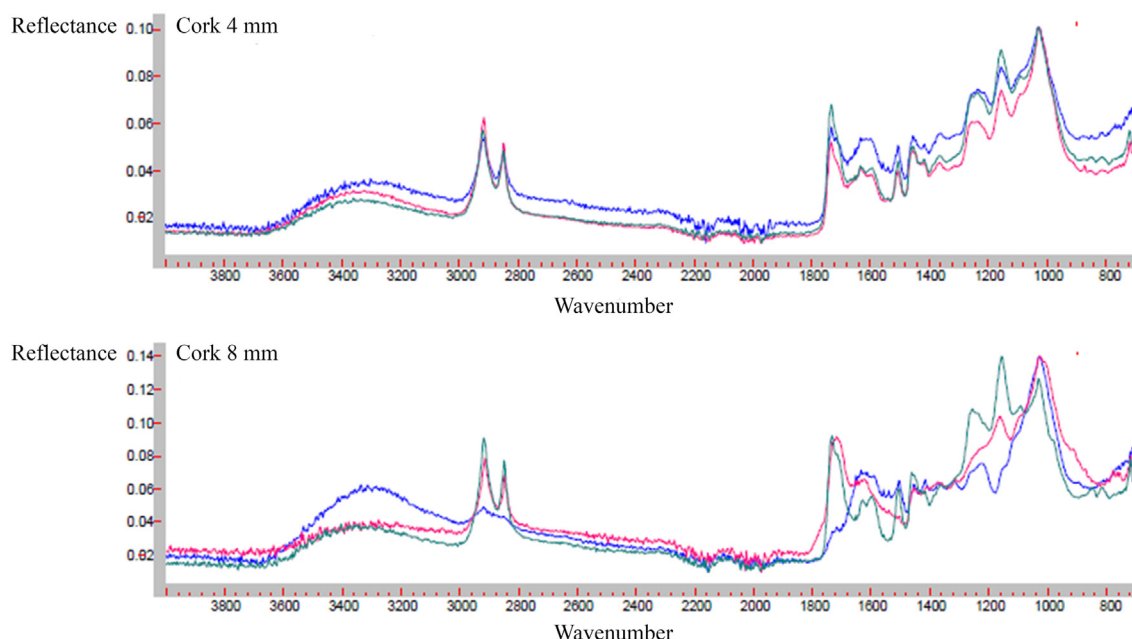

Fig. 1. FTIR results - cork granulate *Quercus suber*.

Table 2
Chemical composition of cork granulates.

Chemical compounds (%)	Species		[a]Extraction part		
	Q. cerris	Q. suber	Cork	Belly	Back
Suberin	[c]28.5	[b]51.3 (±0.2) [c]44.1 [d]38.5	[e]34.4–48.7 [f]33.5–48.7	[e]33.5–53.1	[e]21.1–40.7 [f]21.1–40.7
Total lignin	[c]28.1	[b]14.1 (±0.6) [c]25.7 [d]31.6	[e]14.6–25.3 [f]13.4–31	[e]14.9–31	[e]18.9–28 [f]23.9–27.9
Suberin + lignin	[c]56.6	[b]65.4 [c]69.8 [d]70.1	[e]54.4–71 [f]54.7–71.4	[e]55–69.8	[e]41.6–64 [f]49–64.6

[a] Range: lower and the highest results from different origin area for each extraction part.

[b] Results of the present study. The Standard deviation was calculated with triplicates using the software IBM SPSS (values in brackets).

[c] Adapted from Olivella et al., 2011b.

[d] Adapted from Olivella et al., 2011a.

[e] Adapted from Jové et al., 2011.

[f] Adapted from Olivella et al., 2013a.

This heterogeneous composition confers cork a unique characteristic and makes it a very interesting natural material to investigate (Olivella et al., 2013a). However, not much is known about the influence of the chemical composition of cork on the release of OC.

3.1.3. Elemental analysis

In our samples, carbon was the main element, representing 61.7% of the total mass of the sample, a similar result obtained from other authors (Olivella et al., 2011b), and can correspond to the ranges of cork and belly (extraction parts) founded in literature (Table 3).

The proportion of material coming from belly and cork layers of our samples might be greater than the back layer, justifying the previously mentioned highest content of suberin. In fact, the content of carbon from Q. cerris is slightly lower than the results from Q. suber, which might be related to the lower content of suberin mentioned in the previously section (Table 3).

The organic nitrogen composition might be an issue to be considered in the scope of selecting organic by-products as substrates on NBS for water treatment. The results of Masi et al. (2016) showed an increase of total Kjeldahl nitrogen, which was probably related to the release of organic nitrogen from the substrate (coconut fibber). The organic nitrogen released will be mineralized, and eventually, will change to mineral forms, such as ammonium, nitrates and nitrites. Moreover, the release of greenhouse gases such as CO_2 and N_2O can be increased when organic filter media is used. The increment of organic C and N can lead to higher greenhouse gases emissions in CWs and denitrification process can increase N_2O emissions (Gentile et al., 2008; Maucieri et al., 2017).

Therefore, the nitrogen released from the substrate needs to be addressed during the design of such technologies. In our study, the nitrogen content of cork samples represented <1% and was lower than all results founded in the literature (Table 3), suggesting a low risk regarding the release of organic nitrogen.

3.1.4. PZC

The PZC can be defined as the pH value in which the surface of the biosorbent has zero charge (or the same number of positive and negative charges). Biosorbent surface net charge plays an important role in the sorption/desorption processes, and to explain protonation/deprotonation behaviour in the aqueous medium. As can be seen in Fig. 2, performing the immersion technique, the PZC from granulated cork were between pH 5.5 and 5.8, respectively, to PS 8 mm and 4 mm.

Above pH 6, the surface of the samples is negatively charged, mainly because of the presence of phenolic —OH or carboxylic groups (-COOH). However, the results of Fiol and Villaescusa (2009) showed a PZC of around pH 3,5 regardless the methodology used.

As previously mentioned (Section 3.1) the chemical composition of cork might vary according the species and the extracted part and, therefore, different chemical compositions might lead to different behaviour of protonation/deprotonation process that can influence the PZC.

3.2. Effect of PS and pH on the release of organic carbon

The extractives of cork include several organic compounds such as waxes, triterpenes, fatty acids, glycerides, phenols and polyphenols. The pH influences the chemical speciation, the diffusion rate of solutes, the dissociation of sorbent functional groups and the sorbent surface charge (Rahmani et al., 2010; Glestanifar et al., 2016). It is assumed that the PS affects the release of OC, since it is directly related to surface area, although this effect might vary according to the initial wastewater pH.

Table 3
Elemental composition of cork granulates.

Elements (%)	Species		[a]Extraction part		
	Q. cerris	Q. suber	Cork	Belly	Back
Carbon (C)	[c]50.7	[b]61.7 (±0.97) [c]61	[d]58.5–63.1	[d]60.2–62.5	[d]51.5–59.7
Hydrogen (H)	[c]7.3	[b]7.7 (±0.2) [c]8.7	[d]7.1–8	[d]6.8–9	[d]6.6–7.3
Nitrogen (N)	[c]1.73	[b]0.68 (±0.05) [c]1.7	[d]1.3–2.1	[d]1.3–3.1	[d]1.2–2
Oxygen (O)	[c]31.4	[b]29.8 (±1.14) [c]22.57	[d]26.8–36.1	[d]28.4–36.1	[d]31–42

[a] The range: lower and the highest results from different origin area for each extraction part.

[b] Results of the cork granulated used for this study (Q. Suber). The Standard deviation was calculated with triplicates using the software IBM SPSS (values in brackets).

[c] Adapted from Olivella et al., 2011b.

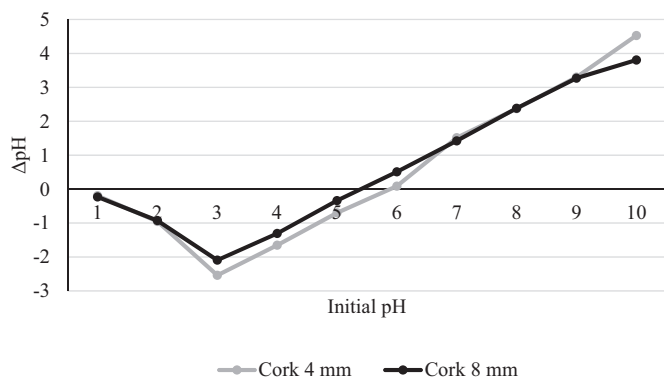[d] Adapted from Olivella et al., 2013b.

Fig. 2. Point of zero charge of cork (4 mm and 8 mm).

The results indicated that the null hypothesis can be rejected for PS ($F_{(1,16)} = 293 > 4.49$, $p = 0.05$) and pH ($F_{(3,16)} = 9.61 > 3.24$, $p = 0.05$), indicating the existence of main effects. On the other hand, there was insufficient evidence to reject the null hypothesis of interaction effect ($F_{(3,16)} = 2.66 < 3.24$, $p = 0.05$). Therefore, the main effects of PS and pH are discussed below (Fig. 3.).

Regardless of the pH, as the PS is smaller the higher the release of OC, due to more available surface area. Regarding the effect of pH, the release was not affected from pH 3 to 7, but a significant effect was obtained from pH 7 to 9 (Tukey HSD, 5%), with higher release at pH = 9, perhaps due to the deprotonation of phenolic —(OH) or carboxylic groups (—COOH) at pH 8–9. No significant interaction effect was obtained ($p = 0.083$). The main effect of PS (95% of the variance) is stronger than the main effect of pH (64% of the variance).

Moreover, 95% of the variance on the release of OC can be attributed to the PS, while 64% was explained by the variance of initial pH, fact, which, suggest that the main effect of PS is stronger than pH. Therefore, comparing each PS across levels of pH, separately, the pH did not affect the release of OC for PS 8 mm. On the other hand, for PS 4 mm, the differences between pH 3–7 and 7–9 were statistically different, decreasing and increasing, respectively. These results might indicate that as lower the PS as greater can be the effect of pH on the release of OC.
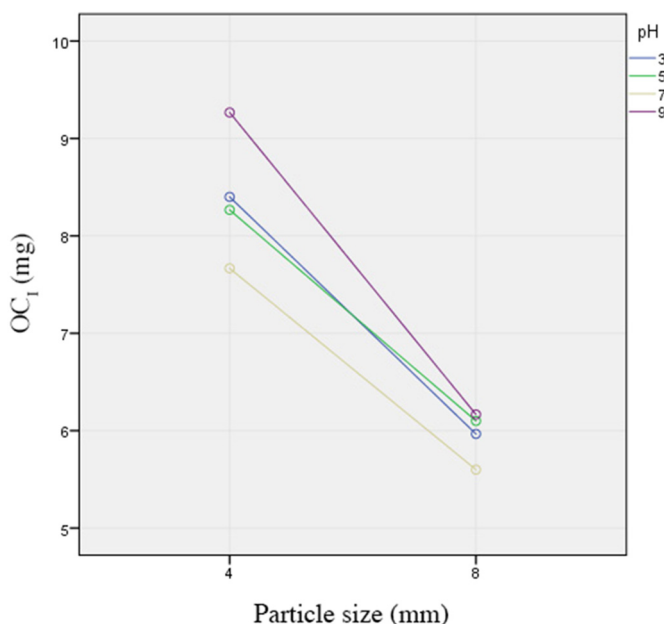
3.3. Kinetics

The null hypothesis can be rejected for PS ($F_{(1,20)} = 931.33 > 4.35$, $p = 0.05$) and CT ($F_{(4,20)} = 232.93 > 2.87$, $p = 0.05$), indicating the existence of main effects of CT and PS on the release of OC. The results showed significant effect of PS and CT on the release of OC, increasing with smaller PS ($p < 0.05$) regardless the CT. Indeed, the mass of carbon released by PS 4 mm was two times higher than the release of OC by PS 8 mm for all CT, except for CT 3 h which was 1.7 time higher. This may indicate the presence of a possible inverse exponential relationship between PS and release of OC.

The post hoc tests (Tukey HSD, 5%) indicate that the multiple comparisons across levels of CT were significant, increasing the release of OC when the CT increases, regardless the PS (Fig. 4). An interaction effect was noticed on the release of OC (PS ∗ CT – $F_{(4,20)} = 28.87 > 2.87$, $p = 0.05$). All eta squared ($\eta2$) were >0.14, indicating that both, main and the interaction effects, are representing great influence on the release of OC. However, while the main effects of PS and CT represents 98% of the release of OC, the interaction effect between then represents 85%, suggesting that the main effects of PS and CT are slightly greater than the interaction effect.

The pairwise comparison results showed no significant differences on the release of OC in the periods, 3–12 h and 12–24 h, for PS 8 mm. However, the release of OC after 24 h was significantly higher than after 3 h. Moreover, there was significant differences between all the means across CT, for PS 4 mm. These results indicate that in the period of 3–12 h and 12–24 h the release of OC was influenced by PS and/or that there is an interaction between the independent variables. This result might indicate that the CT may have a stronger effect on PS 4 mm than on PS 8 mm, in other words, with smaller PS the effect of CT is higher on the release of OC.

Considering the mass of carbon released after 24 h as the total released, it is possible to conclude that approximately 32% and 11% of total carbon released took place during the 3 to 24 h period, respectively for PS 4 mm and PS 8 mm. On the other hand, >70% of the released OC occurred during the first 3 h, for both PS. Therefore, the release of OC might get slower when the CT increases. In addition, this effect might be stronger with the increase of PS. Considering that the specific surface area and PS are inversely related, the surface area might have an effect not just on the amount of carbon released but also at which speed the release of carbon takes place.

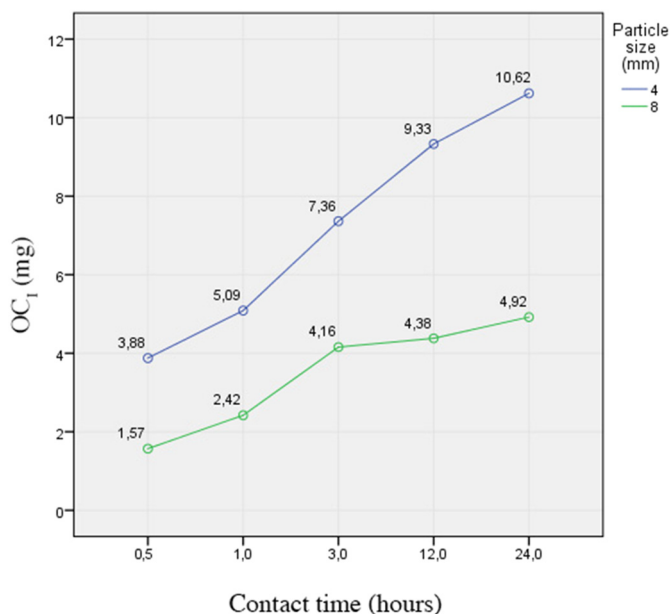Fig. 3. Effect of PS and pH on the release of OC (mg).

Fig. 4. Effect of CT and PS on the release of OC.

Table 4 summarizes the results following the RSM obtained using the software Design Expert® for the best fitted model. Both factors (PS and CT) present significant effect on the response (OC_I) in the range of the study. In this case, the best fitted model is a response surface reduced cubic model which presents interaction between the factors under study (PS and CT) with a p-value < 0.05. In addition, there is a cubic interaction (see factor CT^2PS and p-vales < 0.05 in Table 4). Besides, a quadratic and a cubic effect on the response is presented for the CT factor in the range of the study.

PS factor does not fit in the proper manner when is in quadratic and/or cubic function, for that reason these terms where discarded on the final equation. In addition, it should have been emphasized that the lack of fit is not significant. Consequently, there is only a 0.01% chance that the model occurs due to noise.

All the results derived from the modification of any of the controllable variables can be translated into a predictive mathematical model. This model can quantitatively predict the response within the operating range of controllable variables. It can also give some suitable formulations when a certain response is required. The model only incorporates the statistically significant factors and interactions. Therefore, the mathematical model can be written by the following equation:

$$OC_1(mg) = 5.471 + 2.137 \times CT - 0.506 \times PS - 0.069 \times CT \times PS - 0.163 \times CT^2 + 0.002 \times CT^2 \times PS + 0.004 \times CT^3$$

Fig. 5 presents the surface plot obtained for OC_I. An increase of PS or CT lead to a decrease of OC_I. When both factors are increased their combined effect is found to be lower than the expected form considering the sum of each factor separately. Therefore, it can be concluded that there is significant negative interaction between both factors: as higher the PS the lower the response of OC_I, as we previously explained.

3.4. Cork as an organic carbon source for denitrification

The potential of cork as a carbon source for denitrification was estimated by calculating the amount of carbon released (g) and the amount of water that could be treated in a hypothetical batch biofilter during 24 h. For those calculations, the following assumptions were considered: theoretical stoichiometry for denitrification was considered as 1 g of OC per g nitrate-N (Zhai et al., 2013); two hypothetical batch biofilters with unknown dimensions and a volume of 1 m^3 filled up with each PS of cork (4 mm and 8 mm); the mass of cork for each batch biofilter was calculated considering the density of cork as 123 Kg/m^3 and 125 Kg/m^3 for, respectively, 8 mm and 4 mm PS (Source: internal data from ICSURO). Moreover, the averages of OC_{II} in mg of OC released/g of cork (Section 2.4.3) at 24 h were used for the calculations. The composition of hydroponic wastewater to be treated can be seen in Table 1 and temperature was considered to be the same at lab conditions (Sections 2.3).
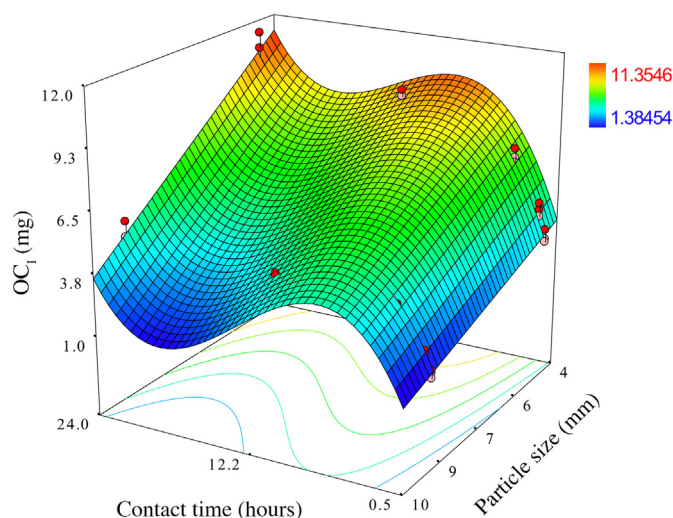

Fig. 5. Kinetics - response surface plot.

Therefore, the chemical release of OC, would be approximately 265 g (PS 4 mm) and 120 g (PS 8 mm) after 24 h. If one considers that all the OC released is consumed by the denitrification process it means that 3.9 m^3 and 1.8 m^3 of hydroponic wastewater could be treated, using PS 4 mm and 8 mm, respectively.

It is well known that PS is a crucial parameter when NBS are designed for wastewater treatment. The PS besides influencing the hydraulics of the system will also affect the performance of contaminants removal by adsorption, complexation and precipitation, as well as the microbiological process; since it influences the biofilm density and growth (Vymazal, 2007). The results mentioned above showed that by using a 4 mm PS, the amount of water treated after 24 h of batch treatment was >2 times that for 8 mm PS. Moreover, results of Capodici et al. (2014) showed that the PS might have a greater influence on OC release than the total OC content itself. The author compared several materials, including cork. Cork presented the lowest result regarding the release of OC, even though it had the highest total OC content. Fact, which were related to its biggest PS of cork in comparison with the other materials. Moreover, the kinetics results of our study highlighted that OC release from cork granulate decreases with time, and this effect is stronger when the PS increase. Therefore, the effect of PS on the release of OC should be considered when NBS treatments are designed using cork as filter media and OC source to enhance denitrification.

In one hand, the chemical release of OC_{III} was <1% of the total content of carbon after 24 h, for both PS, suggesting that cork could be suitable for a long-term carbon organic source (Fig. 6). On the other hand, as mentioned before (Section 3.3), the release of OC gets slower with

Table 4
ANOVA for response surface reduced cubic model.

Factors	Sum of squares	[a]df	Mean square	F-value	[b]cv	[c]ρ-Value
Model	225.73	6	37.62	329.91	2.60	ρ < 0.05
PS	5.10	1	5.10	44.72	4.35	ρ < 0.05
CT	41.45	1	41.45	363.47	4.35	ρ < 0.05
PS ∗ CT	11.57	1	11.57	101.47	4.35	ρ < 0.05
CT^2	8.95	1	8.95	78.49	4.35	ρ < 0.05
CT^2PS	0.99	1	0.99	8.66	4.35	ρ < 0.05
CT^3	12.45	1	12.45	109.23	4.35	ρ < 0.05
Lack of fit	0.33	3	0.11	0.99	3.10	ρ > 0.05
Pure error	2.29	20	0.11	–	–	–
Total	228.36	29	–	–	–	–

[a] df = Degrees of freedon.
[b] Critical value of F distribution.
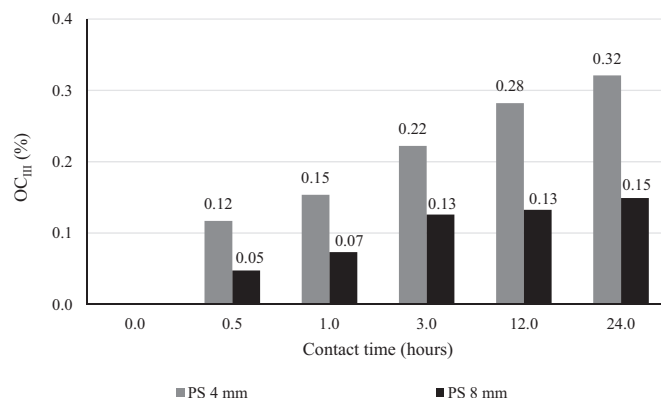[c] ρ < 0.05 = significant. ρ > 0.05 = not significant.

Fig. 6. Effect of CT and PS on the release of OC (%).

time, fact which could be a limitation regarding cork long-term efficiency as carbon source. In the present study, after 24 h, for PS 4 mm and 8 mm respectively, 2.12 and 0.98 mg of OC was released per g of cork. Capodici et al. (2014) results showed that, after 50 h a peak of carbon release was reached being 5.6 mg of OC/g of cork. After 50 h the increment of carbon released was slower and linear. Those results suggest that even though the OC release gets slower with time it keeps taking place, fact which highlight the importance of models to predict it.

However, it is important to consider that the performance of cork as carbon source will be influenced by real scale features such as, type of treatment (bio filters, CWs, green walls and others), design and operational factors (flow type, saturated or unsaturated conditions, retention time, hydraulic and pollutants load, among others), cork features (chemical composition) and environmental conditions (temperature, pH). Therefore, further studies on long-term efficiency of cork as an OC source are needed.

3.5. An issue to be regarded: phenolic compounds release

Several phenolic compounds are persistent pollutants with high toxicity even at low concentrations (Villegas et al., 2016), and their accumulation in the environment can lead to biodiversity loss and to increase human health risk (Sun et al., 2015; Stefanakis and Thullner, 2016; Villegas et al., 2016).

Phenolic compounds were not measured in the present study, although this potential issue needs to be addressed once the use of cork as filter media in NBS may lead to an increase of biorecalcitrants (phenolic compounds) in the effluent. For example, the cork boiling water, which is acquired after the raw cork granulate is boiled up to 1.5 h, have high organic load of biorecalcitrant compounds, resulting in an increase of chemical oxygen demand and total phenolic compounds (TPC) concentration (Gomes et al., 2018). Moreover, the TPC of the cork boiling water can vary from 1.0–3.5 g/L, which is substantially high when compared to the toxicity range for phenolic compounds which is 0.009–0.025 g/L (Kulkarni and Kaware, 2013; Gomes et al., 2018).

In this regard, NBS, such as CWs, have been proposed as an economic and environmentally friendly treatment to remove phenolic compounds from wastewaters (Kurzbaum et al., 2010; Stefanakis and Thullner, 2016; Gomes et al., 2018). The main removal mechanisms of phenolic compounds taking place in CWs are sorption, phytoremediation (plant uptake) and volatilization, although biodegradation seem to be the key removal process of phenolic compounds in this type of treatment (Imfeld et al., 2009; Stefanakis and Thullner, 2016; Gomes et al., 2018).

In one hand, biodegradation of phenolic compounds taking place in NBS could overcome the issue related to the release of phenolics by cork. The results from Kurzbaum et al. (2010) showed that in a subsurface flow CW, most of phenolic compounds removal was due to bacterial colonization of roots and gravel bed, while abiotic processes like evaporation and adsorption were considered negligible. Gomes et al. (2018), studied the removal of phenolic compounds from cork boiled water using a horizontal subsurface flow CWs (lab scale). The removal achieved was higher than conventional biological treatment, suggesting the great potential of this type of treatment regarding the removal of phenolic compounds released by cork. However, both authors used conventional substrates like gravel (Kurzbaum et al., 2010) and light expanded clay (Gomes et al., 2018), while not much is known about the increment of phenolic compounds when cork is used as substrate in NBS treating wastewaters.

On the other hand, Calheiros et al. (2018) studied micro biodiversity of treatment wetland treating winery wastewater using cork stoppers as substrate (granulate 3–7 mm), what means a double load of phenolic compounds, since winery wastewaters have high concentration of polyphenols. The author results showed that the gender *Pseudomonas* spp. and *Bacillus* spp. were dominant and most important they were able to survive in such conditions. According to Nair et al. (2008) *Pseudomonas* spp. and *Bacillus* spp. are efficient at biodegrading phenolic

compounds. This might suggest that despite the toxic effect of phenolic compounds on microbial communities, the expected release of phenolic compounds from cork could be compensated by biodegradation occurring in NBS such as CWs.

However, three aspects need to be highlighted. First, biodegradation of phenolic compounds is a complex process. Besides depending on the composition and structure of the phenolic compounds is also strongly affected by environmental conditions such as pH, temperature and dissolved oxygen (Zhao et al., 2018). Secondly, cork is a heterogenic material regarding its chemical constitution. As was discussed previously (Section 3.1.2), the chemical constitution of cork might vary according with the species and extraction part, fact which might influence the types of phenolic compounds released. Thirdly, depending on the stage of cork acquirement (raw cork or after boiling process) the chemical properties will be certainly different. Perhaps, the reuse of cork granulates generated during the production of stoppers or even the stoppers themselves, would be a saver alternative, since both passed by boiling process which extracts most of phenolic compounds.

Therefore, the release of phenolic compounds needs to be considered, when design NBS using cork as substrate and "internal" OC source. Moreover, laboratory and real scale studies focused on understanding and overcoming this limitation are recommended to ensure safe reuse of cork as substrate in NBS.

4. Conclusions

The main compound and element of cork are Suberin and carbon, representing respectively, >50% and 60% of the sample composition. Also, when comparing the results with other researches, it was noticed that might be a variance on the content of suberin across species, within the same species and depending on the extraction part (Belly, cork and back). Furthermore, the lignin content seems to vary within *Q. suber* specie. However, no statistical analysis was performed to validate this hypothesis. Nevertheless, as not much is known about the influence of the chemical composition of cork on the release of OC, further researches on it might facilitate standards to ensure an efficient performance of cork as carbon source in accordance with its chemical constitution.

The PZC of cork was between pH 5 and 6, which was different than the result founded in literature (3.5). This difference was attributed to the variance of cork chemical composition which might lead to different behaviour of protonation/deprotonation.

As smaller the PS granulometry the higher is the OC released, regardless the pH or CT. Regarding the pH main effect, the results suggest that as lower the PS as stronger the effect of pH on the release of OC. The kinetics results showed that as the CT increases the release of OC is increased as well, regardless the PS. However, an interaction effect between PS and CT was noticed, indicating that as smaller the PS becomes the higher the effect of CT has on the release of OC. In addition, >70% of the carbon released took place during the first 3 h for both PS, indicating that the release of OC might get slower as CT increases. Those results highlight the effect of surface area affects the amount carbon released and as well the velocity that the carbon is released.

When using cork as carbon source of NBS treating wastewater, the effect of PS on the release of OC can play an important role at designing such systems. Estimations showed that the amount of water treated by using PS 4 mm was >2 times that would be for PS 8 mm, considering that all carbon released would be consumed by denitrification. In this regard, the results of surface response methodology indicate that optimization could be performed to facilitate the design of technologies considering the interaction between PS and CT at releasing OC.

Using cork as a source of carbon for denitrification seems to be a promising alternative to reduce costs and environmental hazard of NBS treating wastewaters with low carbon content and high nitrates. By using organic substrates, the development of microbiota also might be facilitated and thus, microbiological removal process. However, this

practice might lead to losses of hydraulic conductivity and adsorption surface area, fact that can influence treatment efficiency. Indeed, at real scale and long-term conditions cork behaviour at releasing OC will be affected by external factor (type of treatment, design and operation factors, cork features and environmental conditions).

The release of phenol compounds by cork can be a restriction for using the material as filter media in NBS. However, the biodegradation of such compounds seems to be efficient in NBS, fact which could help overcome this restriction. Indeed, using cork granule acquired after boiling process might reduce the risk of releasing phenolic compounds in NBS treating wastewaters.

Validating the use of cork as a carbon source for denitrification at real and long-term scales can be an interesting line of research. Furthermore, the effect of such practice on the release of greenhouse gases and phenolic compounds also should be considered. Nerveless, the reuse of organic by-products as filter media seems to be an environmental and economic friendly alternative to enhance denitrification in NBS. This approach can help preserve natural capital, reduce the dependency of external inputs, treatment costs, increase self-efficiency, all of it leading to a sustainable technological development in the scope of wastewater treatments.

Acknowledgements

References

Abbassi, B., Al-Zboon, K., Radaideh, J., Wahbeh, A., 2011. Using constructed wetlands to improve drainage water quality from hydroponics farms. Irrig. Drain. 60, 370–380. https://doi.org/10.1002/ird.580.

Capodici, M., Morici, C., Viviani, G., 2014. Batch test evaluation of four organic substrates suitable for biological groundwater denitrification. Chem. Eng. Trans. 38, 43–48. https://doi.org/10.3303/CET1438008.

Chang, J., Ma, L., Chen, J., Lu, Y., Wang, X., 2016. Greenhouse wastewater treatment by baffled subsurface-flow constructed wetlands supplemented with flower straws as carbon source in different modes. Environ. Sci. Pollut. Res. 24, 1578–1587. https://doi.org/10.1007/s11356-016-7922-4.

Chen, Z.J., Tian, Y.H., Zhang, Y., Song, B.R., Li, H.C., Chen, Z.H., 2016. Effects of root organic exudates on rhizosphere microbes and nutrient removal in the constructed wetlands. Ecol. Eng. 92, 243–250. https://doi.org/10.1016/j.ecoleng.2016.04.001.

Cordeiro, N., Belgacem, M.N., Silvestre, A.J.D., Pascoal Neto, C., Gandini, A., 1998. Cork suberin as a new source of chemicals. 1. Isolation and chemical characterization of its composition. Int. J. Biol. Macromol. 22, 71–80. https://doi.org/10.1016/S0141-8130(97)00090-1.

Crespo-Alonso, M., Nurchi, V.M., Biesuz, R., Alberti, G., Spano, N., Pilo, M.I., Sanna, G., 2013. Biomass against emerging pollution in wastewater: ability of cork for the removal of ofloxacin from aqueous solutions at different pH. J. Environ. Chem. Eng. 1, 1199–1204. https://doi.org/10.1016/j.jece.2013.09.010.

Domingues, V., Alves, A., Cabral, M., Delerue-Matos, C., 2005. Sorption behaviour of bifenthrin on cork. J. Chromatogr. 1069, 127–132. https://doi.org/10.1016/j.chroma.2004.10.011.

Dordio, A.V., Goncalves, P., Texeira, D., Candeias, A.J., Castanheiro, J.E., Pinto, A.P., Carvalho, A.J.P., 2011. Pharmaceuticals sorption behaviour in granulated cork for the selection of a support matrix for a constructed wetlands system. Int. J. Environ. Anal. Chem. 91, 615–631. https://doi.org/10.1080/03067319.2010.510605.

Dunets, C.S., Zheng, Y., Dixon, M., 2015. Use of phosphorus-sorbing materials to remove phosphate from greenhouse wastewater. Environ. Technol. 36, 1759–1770. https://doi.org/10.1080/09593330.2015.1009497.

Fiol, N., Villaescusa, I., 2009. Determination of sorbent point zero charge: usefulness in sorption studies. Environ. Chem. Lett. 7, 79–84. https://doi.org/10.1007/s10311-008-0139-0.

Formosa, J., Chimenos, J.M., Lacasta, A.M., Niubo, M., 2012. Interaction between low-grade magnesium oxide and boric acid in chemically bonded phosphate ceramics formulation. Ceram. Int. 38, 2483–2493. https://doi.org/10.1016/j.ceramint.2011.11.017.

Gagnon, V., Maltais-Landry, G., Puigagut, J., Chazarenc, F., Brisson, J., 2010. Treatment of hydroponics wastewater using constructed wetlands in winter conditions. Water Air Soil Pollut. 212, 483–490. https://doi.org/10.1007/s11270-010-0362-8.

Gentile, R., Vanlauwe, B., Chivenge, P., Six, J., 2008. Interactive effects from combining fertilizer and organic residue inputs on nitrogen transformations. Soil Biol. Biochem. 40, 2375–2384. https://doi.org/10.1016/j.soilbio.2008.05.018.

Glestanifar, H., Asadi, A., Alinezhad, A., Haybati, B., Vosoughi, M., 2016. Isotherm and kinetic studies on the adsorption of nitrate onto nanoalumina and iron-modified pumice. Desalin. Water Treat. 57, 5480–5487. https://doi.org/10.1080/19443994.2014.1003975.

Gomes, A.C., Silva, L., Albuquerque, A., Simões, R., Stefanakis, A.I., 2018. Investigation of lab-scale horizontal subsurface flow constructed wetlands treating industrial cork boiling wastewater. Chemosphere 207, 430–439. https://doi.org/10.1016/j.chemosphere.2018.05.123.

Gruyer, N., Dorais, M., Zagury, G.J., Alsanius, B.W., 2013. Removal of plant pathogens from recycled greenhouse wastewater using constructed wetlands. Agric. Water Manag. 117, 153–158. https://doi.org/10.1016/j.agwat.2012.11.009.

Hafshejani, L.D., Hooshmand, A., Naseri, A.A., Mohammadi, A.S., Abbasi, F., Bhatnagar, A., 2016. Removal of nitrate from aqueous solution by modified sugarcane bagasse biochar. Ecol. Eng. 95, 101–111. https://doi.org/10.1016/j.ecoleng.2016.06.035.

Huett, D.O., Morris, S.G., Smith, G., Hunt, N., 2005. Nitrogen and phosphorus removal from plant nursery runoff in vegetated and unvegetated subsurface flow wetlands. Water Res. 39, 3259–3272. https://doi.org/10.1016/j.watres.2005.05.038.

Imfeld, G., Braeckevelt, M., Kuschk, P., Richnow, H.H., 2009. Monitoring and assessing processes of organic chemicals removal in constructed wetlands. Chemosphere 74, 349–362. https://doi.org/10.1016/j.chemosphere.2008.09.062.

Jové, P., Olivella, M.À., Cano, L., 2011. Study of the variability in chemical composition of bark layers of Quercus suber L. from different production areas. Bioresources 6, 1806–1815. https://doi.org/10.15376/biores.6.2.1806-1815.

Koide, S., Satta, N., 2004. Separation performance of ion-exchange membranes for electrolytes in drainage nutrient solutions subjected to electrodialysis. Biosyst. Eng. 87, 89–97. https://doi.org/10.1016/j.biosystemseng.2003.09.005.

Krika, F., Benlahbib, O. el F., 2015. Removal of methyl orange from aqueous solution via adsorption on cork as a natural and low-coast adsorbent: equilibrium, kinetic and thermodynamic study of removal process. Desalin. Water Treat. 53, 3711–3723. https://doi.org/10.1080/19443994.2014.995136.

Kulkarni, S.J., Kaware, J.P., 2013. Review on research for removal of phenol from wastewater. Int. J. Sci. Res. Publ. 3, 1–5.

Kurzbaum, E., Zimmels, Y., Kirzhner, F., Armon, R., 2010. Removal of phenol in a constructed wetland system and the relative contribution of plant roots, microbial activity and porous bed. Water Sci. Technol. 62, 1327–1334. https://doi.org/10.2166/wst.2010.399.

Marques, A., Pereira, H., Meier, D., Faix, O., 1994. Quantitative analysis of cork (Quercus suber L.) and milled cork lignin by FTIR spectroscopy, analytical pyrolysis, and total hydrolysis. Holzforschung https://doi.org/10.1515/hfsg.1994.48.s1.43.

Masi, F., Bresciani, R., Rizzo, A., Edathoot, A., Patwardhan, N., Panse, D., Langergraber, G., 2016. Green walls for greywater treatment and recycling in dense urban areas: a case-study in Pune. J. Water Sanit. Hyg. Dev. 6, 342–347. https://doi.org/10.2166/washdev.2016.019.

Maucieri, C., Barbera, A.C., Vymazal, J., Borin, M., 2017. A review on the main affecting factors of greenhouse gases emission in constructed wetlands. Agric. For. Meteorol. 236, 175–193. https://doi.org/10.1016/j.agrformet.2017.01.006.

Miranda, I., Gominho, J., Pereira, H., 2013. Cellular structure and chemical composition of cork from the Chinese cork oak (Quercus variabilis). J. Wood Sci. 59, 1–9. https://doi.org/10.1007/s10086-012-1300-8.

Montgomery, D.C., 2012. Design and Analysis of Experiments. eighth ed. John Wiley & Sons, Inc.

Mutsvangwa, C., Matope, E., 2017. Use of an external organic carbon source in the removal of nitrates in bio-sand filters (BSFs). Drink. Water Eng. Sci. 10, 119–127. https://doi.org/10.5194/dwes-10-119-2017.

Nair, C.I., Jayachandran, K., Shashidhar, S., 2008. Biodegradation of phenol. Afr. J. Biotechnol. 7, 4951–4958. https://doi.org/10.5897/AJB08.087.

Nordström, A., Herbert, R., 2017. Field-scale denitrifying woodchip bioreactor treating high nitrate mine water at low temperatures. In: Wolkersdorfer, C., Sartz, L., Sillanpää, M., Häkkinen, A. (Eds.), 13th International Mine Water Association Congress – Mine Water & Circular Economy. LUT Press, Lappeenranta, pp. 1087–1094.

Olivella, M.À., Jové, P., Oliveras, A., 2011a. The use of cork waste as a biosorbent for persistent organic pollutants-study of adsorption/desorption of polycyclic aromatic hydrocarbons. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. 46, 824–832. https://doi.org/10.1080/10934529.2011.579845.

Olivella, M.À., Jové, P., Pereira, H., Villaescusa, I., Fiol, N., 2011b. Sorption performance of Quercus cerris cork with polycyclic aromatic hydrocarbons and toxicity testing. Bioresources 6, 3363–3375.

Olivella, M.À., Fernández, I., Cano, L., Jové, P., Oliveras, A., 2013a. Role of chemical components of cork on sorption of aqueous polycyclic aromatic hydrocarbons. Int. J. Environ. Res. 7, 225–234. https://doi.org/10.22059/IJER.2012.601.

Olivella, M.À., Jové, P., Bianchi, A., Bazzicalupi, C., Cano, L., 2013b. An integrated approach to understanding the sorption mechanism of phenanthrene by cork. Chemosphere 90, 1939–1944. https://doi.org/10.1016/j.chemosphere.2012.10.035.

Ortega-Fernández, C., González-Adrados, J.R., García-Vallejo, M.C., Calvo-Haro, R., Cáceres-Esteban, M.J., 2006. Characterization of surface treatments of cork stoppers by FTIR-ATR. J. Agric. Food Chem. 54, 4932–4936. https://doi.org/10.1021/jf0529823.

Park, J.B.K., Craggs, R.J., Sukias, J.P.S., 2008. Treatment of hydroponic wastewater by denitrification filters using plant prunings as the organic carbon source. Bioresour. Technol. 99, 2711–2716. https://doi.org/10.1016/j.biortech.2007.07.009.

Park, J.B.K., Craggs, R.J., Sukias, J.P.S., 2009. Removal of nitrate and phosphorus from hydroponic wastewater using a hybrid denitrification filter (HDF). Bioresour. Technol. 100, 3175–3179. https://doi.org/10.1016/j.biortech.2009.01.036.

Park, J.-H., Kim, S.H., Delaune, R.D., Cho, J.S., Heo, J.-S., Ok, Y.S., Seo, D.-C., 2015. Enhancement of nitrate removal in constructed wetlands utilizing a combined autotrophic and heterotrophic denitrification technology for treating hydroponic wastewater containing high nitrate and low organic carbon concentrations. Agric. Water Manag. 162, 1–14. https://doi.org/10.1016/j.agwat.2015.08.001.

Pescod, M.B., 1992. Wastewater characteristics and effluent quality parameters. In: Pescod, M.B. (Ed.), Wastewater Treatment and Use in Agriculture - FAO Irrigation and Drainage Paper 47. FAO, Rome, pp. 7–25.

Pintor, A.M.A., Ferreira, C.I.A., Pereira, J.C., Correia, P., Silva, S.P., Vilar, V.J.P., Botelho, C.M.S., Boaventura, R.A.R., 2012. Use of cork powder and granules for the adsorption of pollutants: a review. Water Res. 46, 3152–3166. https://doi.org/10.1016/j.watres.2012.03.048.

Prades, C., García-Olmo, J., Romero-Prieto, T., García de Ceca, J.L., López-Luque, R., 2010. Methodology for cork plank characterization (*Quercus suber* L.) by near-infrared spectroscopy and image analysis. Meas. Sci. Technol. 21, 11. https://doi.org/10.1088/0957-0233/21/6/065602.

Prodanovic, V., Hatt, B., McCarthy, D., Zhang, K., Deletic, A., 2017. Green walls for greywater reuse: understanding the role of media on pollutant removal. Ecol. Eng. 102, 625–635. https://doi.org/10.1016/j.ecoleng.2017.02.045.

Prystay, W., Lo, K.V., 2001. Treatment of greenhouse wastewater using constructed wetlands. J. Environ. Sci. Health B 36, 341–353. https://doi.org/10.1081/PFC-100103574.

Rahmani, A., Mousavi, H.Z., Fazli, M., 2010. Effect of nanostructure alumina on adsorption of heavy metals. Desalination 253, 94–100. https://doi.org/10.1016/j.desal.2009.11.027.

Sierra-Pérez, J., Boschmonart-Rives, J., Dias, A.C., Gabarrell, X., 2016. Environmental implications of the use of agglomerated cork as thermal insulation in buildings. J. Clean. Prod. 126, 97–107. https://doi.org/10.1016/j.jclepro.2016.02.146.

Stefanakis, A.I., Thullner, M., Ansari, A., Gill, S., Gill, R., Lanza, G., 2016. Fate of phenolic compounds in constructed wetlands treating contaminated water. Phytoremediation. Springer, Cham, pp. 311–325 https://doi.org/10.1007/978-3-319-41811-7.

Sun, X., Wang, C., Li, Y., Wang, W., Wei, J., 2015. Treatment of phenolic wastewater by combined UF and NF/RO processes. Desalination 355, 68–74. https://doi.org/10.1016/j.desal.2014.10.018.

Taylor, M.D., White, S.A., Chandler, S.L., Klaine, S.J., Whitwell, T., 2006. Nutrient management of nursery runoff water using constructed wetland systems. HortTechnology 16, 610–614.

Villegas, L.G.C., Mashhadi, N., Chen, M., Mukherjee, D., Taylor, K.E., Biswas, N., 2016. A short review of techniques for phenol removal from wastewater. Curr. Pollut. Reports 2, 157–167. https://doi.org/10.1007/s40726-016-0035-3.

Vymazal, J., 2007. Removal of nutrients in various types of constructed wetlands. Sci. Total Environ. 380, 48–65. https://doi.org/10.1016/j.scitotenv.2006.09.014.

Wen, Y., Chen, Y., Zheng, N., Yang, D., Zhou, Q., 2010. Effects of plant biomass on nitrate removal and transformation of carbon sources in subsurface-flow constructed wetlands. Bioresour. Technol. 101, 7286–7292. https://doi.org/10.1016/j.biortech.2010.04.068.

Wu, H., Wang, X., He, X., Zhang, S., Liang, R., Shen, J., 2017. Effects of root exudates on denitrifier gene abundance, community structure and activity in a micro-polluted constructed wetland. Sci. Total Environ. 598, 697–703. https://doi.org/10.1016/j.scitotenv.2017.04.150.

Zhai, X., Piwpuan, N., Arias, C.A., Headley, T., Brix, H., 2013. Can root exudates from emergent wetland plants fuel denitrification in subsurface flow constructed wetland systems? Ecol. Eng. 61, 555–563. https://doi.org/10.1016/j.ecoleng.2013.02.014.

Zhang, M., Zhao, L., Mei, C., Yi, L., Hua, G., 2014. Effects of plant material as carbon sources on TN removal efficiency and N_2O flux in vertical-flow-constructed wetlands. Water Air Soil Pollut. 225, 1–11. https://doi.org/10.1007/s11270-014-2181-9.

Zhao, L., Wu, Q., Ma, A., 2018. Biodegradation of phenolic contaminants: current status and perspectives. IOP Conf. Ser. Earth Environ. Sci 111, pp. 1–5. https://doi.org/10.1088/1755-1315/111/1/012024.